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(54) SPHERIC POROUS SILICA OR SILICA/METAL COMPOSITE PARTICLE AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide spheric porous silica or silica/metal composite particles expressed by specified formula, having 0.1 to 500 μm particle size and substantially 1 sphericity obtained by a circumcircle method, and showing an X-ray diffraction peak from 1 to 5° for (Cu-Kα) and a maximum pore volume at a pore diameter from 15 to 40 Å, and to provide a method for manufacturing the particles.
SOLUTION: The spheric porous silica or silica/metal composite particles are obtained by adding water or an acidic aqueous solution while stirring to a mixture liquid containing a water-miscible organic solvent, alkylamines and silicates or a combination of silicates and metal salts soluble with the water- miscible organic solvent to produce a silica-alkylamine composite product, growing the product into spheric particles, and removing the alkylamines in the spheric particles.

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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the spherical porosity silica which adds water or aqueous acids under stirring into mixed liquor including the combination of a water miscibility organic solvent, alkylamine and silicate ester or silicate ester, and a metal salt meltable to a water miscibility organic solvent, and is characterized by growing up the silica-alkylamine compound product to generate into a spherical particle, and removing the alkylamine in a spherical particle thru/or a silica metal complex particle.
[Claim 2] the manufacture approach according to claim 1 that M expresses polyvalent metal among following type SiO2 and nMOm / 2 types, m is the valence of polyvalent metal, and a spherical porosity silica thru/or a silica metal complex particle are characterized by n having the chemical presentation it is [presentation] 0.1 or less number containing zero and which is come out of and expressed.
[Claim 3] The manufacture approach according to claim 1 or 2 characterized by having the particle diameter a spherical porosity silica thru/or whose silica metal complex particle are 0.1 thru/or 500 micrometers.
[Claim 4] The manufacture approach given in claim 1 thru/or any of 3 they are. [which is characterized by using silicate ester and alkylamine by the mole ratio of 1:0.1 thru/or 1:0.8]
[Claim 5] The manufacture approach given in claim 1 thru/or any of 4 they are. [which is characterized by using a water miscibility organic solvent per / 0.05 / one mol of silicate ester thru/or in the amount of ten mols]
[Claim 6] The manufacture approach given in claim 1 thru/or any of 5 they are. [which is characterized by adding water per / 20 / one mol of silicate ester thru/or in the amount of 100 mols]
[Claim 7] The manufacture approach given in claim 1 thru/or any of 6 they are. [which is characterized by using an acid in the amount of 0.15 mols or less per one mol of silicate ester]
[Claim 8] The manufacture approach given in claim 1 thru/or any of 7 they are. [which is characterized by a water miscibility organic solvent being alcohol of univalent thru/or many **]
[Claim 9] The manufacture approach given in claim 1 thru/or any of 8 silicate ester is in a carbon number. [which is characterized by being silicate ester of the alcohol of 1 thru/or 4]
[Claim 10] M expresses polyvalent metal among following type SiO2 and nMOm / 2 types, and m is the valence of polyvalent metal. n is the spherical porosity silica thru/or silica metal complex particle which is 0.1 or less number containing zero and which comes out and has the chemical presentation expressed. The sphericity for which is in the range whose particle size is 0.1 thru/or 500 micrometers, and it asked by the circumscribed circle method is parenchyma top 1. The spherical porosity silica thru/or silica metal complex particle characterized by having an X diffraction peak at an angle of diffraction 1 thru/or 5 times (Cu-Kalpha), and having the maximal value of pore volume in a pole diameter 15 thru/or 40A.
[Claim 11] The spherical porosity silica according to claim 10 thru/or silica metal complex particle characterized by for said spherical particle seeing with a scanning electron microscope photograph, and consisting of a parenchyma top monodisperse particle.
[Claim 12] The catalyst or catalyst support characterized by consisting of a spherical porosity silica according to claim 10 or 11 thru/or a silica metal complex particle.
[Claim 13] The deodorant characterized by consisting of a spherical porosity silica according to claim 10 or 11 thru/or a silica metal complex particle.
[Claim 14] The gas conditioning agent characterized by consisting of a spherical porosity silica according to claim 10 or 11 thru/or a silica metal complex particle.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a spherical porosity silica thru/or a silica metal complex particle, and its manufacture approach. A silicon alkoxide is used more for a detail as silicate ester. And Ti which uses the metal salt which dissolved into the alcoholic solution of the silica dissolved kind to generate and a silica dissolved kind, and a water miscibility organic solvent as a raw material, In the solution phase which contains simultaneously one kind or plurality of various metal dissolved kinds, such as Zr, aluminum, Fe, Zn, Cr, Mn, Co, Cu, nickel, V, and Sn The spherical porosity silica metal complex particle which contains the spherical porosity silica particle of diameter micron order, or one or more kinds besides Si of metallic elements while it has the pore arranged regularly based on the order organization potency of alkylamine, it is the manufacturing method and is related with the spherical porosity silica which was suitable for the ingredient useful to industry and environmental protection etc. as a catalyst for decomposition thru/or a silica metal complex particle, and its manufacturing method at adsorption / separation pan of a shape selectivity catalyst, adsorption, separation and the conservative of useful ion and a molecule, and a harmful ion and a molecule.
[0002]
[Description of the Prior Art] Porous body MCM-41 and the synthesis method which carried out the regulation array are especially mentioned as discovery with the 2-10nm meso hole exciting to the shape of a honeycomb announced in the Nature paper in the history of foam development in 1992. Since the discovery, research of meso pore foam has been accelerated at a stretch, and the application to the clathrate compound which has the light which used the regulation array of the functional molecule in a meso hole only as a catalyst based on molecule sieve nature, the MAG, and an electric function has also been considered. Furthermore, recently, development of the meso foam of not only the regularity of a meso hole but the shape of fibrous and the globular shape which controlled the macro gestalt of centimeter size from the micron, a hollow globular shape, tabular, or a thin film attracts attention.
[0003] Many researches are reported about the spherical porosity silica concerning this invention. For example;
(1) Schacht, S.; Huo, Q.; Voigt-Martin, I.G.; Stucky, G.D.; To "Science, 1996, 273, and 768.", such as Schuth and F. In the CTAB (cetyl trimethylammonium bromide) water solution which added the hydrochloric acid In case the tetraethyl alt.silicate (TEOS) containing a mesitylene is dropped, the hollow-like spherical porosity silica particle of micron order generates by controlling agitating speed, (2) Huo, Q.; Feng, J.; Schuth, F.; To "Chem.Mater.1997, 9, and 14.", such as Stucky and G.D. If tetrabuthyl alt.silicate (TBOS) is added and stirred at CTAB in water and the solution which added NaOH etc., a spherical silica porous body with a particle size of 0.1-2mm is producible. By this approach, transition metals, such as Cu, Co, Ti, Zr, and V, can be introduced into a silica frame, (3) Grun, M.; Lauer, I.; To "Adv.Mater.1997, 9, and 254.", such as Unger and K.K. By adding TEOS, adding cation mold surfactant water solutions, such as CTAB, to aqueous ammonia / ethanol mixed solution, and stirring them That a 0.4-1.1-micrometer spherical particle is obtained, (4) Yang, H.; Vovk, G.; Coombs, N.; Sokolov, I.; To "Mater.Chem.1998, 8, and 743.", such as Ozin and G.A.J. By controlling the mixed rate of CTAC (cetyl trimethylammonium chloride), TEOS, and a low-concentration hydrochloric-acid water solution A spherical particle with a diameter of 1-10 micrometers is compounded in the bottom of static conditions, and 80 degrees C and seven - ten days, (5) Qi, L.; Ma, J.; Cheng, H.; To "Chem.Mater.1998, 10, and 1623.", such as Zhao and Z. By hydrolyzing TEOS under static conditions in the low-concentration hydrochloric-acid water solution in which the mixed surfactant of CTAB and the deca ethylene glycol MONOHEKISADESHIRU ether (C16EO10) was dissolved

Producing a spherical silica meso porous body with a diameter of 2-6 micrometers, (6) Lin, H.P.; Cheng, Y.R.; To "Chem.Mater.1998, 10, 3772.", such as Mou and C.Y. Where it added the butanol to MIKISU chill trimethylammonium bromide (C14TMAB) and a specific silicate and 2 phase separation is made them If a hydrochloric-acid water solution is dropped, the hollow-like spherical silica meso porous body which has a special internal structure with a diameter of 4-6 micrometers will generate, (7) Singh, P.S.; To "Chem.Lett.1998 and 101.", such as Kosuge and K. When a straight chain octyl amine is added stirring in the mixed solution of TEOS and a hydrochloric-acid water solution, with the mixing ratio The spherical silica meso porous body with a diameter [of the shape of the shape of hollow or a spiral] of 1-6 micrometers from which the thickness of a spherical shell differs is compounded, (8) -- Boissiere and C.; van der Lee and A.; El Mansouri and A.; Larbot and A.; Prouzet and E. etc. -- to "Chem.Commun.1999 and 2047." In order to mix TEOS with a straight chain nonionic polyoxyethylene and to advance condensation of a silica after adding a hydrochloric acid further, Add a sodium fluoride, it is made to react for three days, and a spherical silica meso porous body with a diameter of 10 micrometers or less is compounded, (9) Boissiere, C.; Larbot, A.; To "Chem.Mater.2000, 12, 1937.", such as Prouzet and E. After dissolving a straight chain nonionic polyoxyethylene in a hydrochloric-acid water solution and holding at 2 degrees C, a specific silicate solution is added and it warms at 20-70 degrees C. Furthermore, in order to advance condensation of a silica, add a sodium fluoride, it is made to react for three days, and compounding a spherical silica meso porous body with a diameter of about 5 micrometers is indicated. (10) Gallis, KW.; Araujo, J.T.; Duff, K.J.; Moore, J.G.; To "Adv.Mater.1999, 11, and 1452.", such as Landry and C.C. Obtaining [a spherical silica meso porous body with a diameter of 4-10 micrometers] ** is indicated by by heating TEOS at 150 degrees C after 1-hour stirring for 40 minutes in addition to the CTAB solution which dissolved in dilute hydrochloric acid.

[0004] Moreover, after mixing alkoxysilane, water, a surfactant, and an acid in a publication-number No. 328558 [ten to] official report and carrying out the condensation reaction of the alkoxysilane to it, this reaction mixture is poured into the organic solvent which added alkali, and after generating a spherical-like ** silica / surfactant complex, the manufacture approach of a spherical meso porous body is indicated by by removing that surfactant from this silica / surfactant complex ejection and after that in this.

[0005] Furthermore, this invention person etc. compounded the spherical silica base meso porous body which contained the metal component in the mixed liquor of TEOS and straight chain alkylamine in the same procedure by being adding a hydrochloric-acid water solution, compounding a spherical silica meso porous body with a diameter of 5-300 micrometers, and producing a mixed solution with TEOS further using the metal alkoxide which is in a solution condition in ordinary temperature. Moreover, the spherical silica base meso porous body was compounded by dissolving and pre-using a metal salt into straight chain alkylamine or a hydrochloric-acid water solution. (Patent pending)

[0006]

[Problem(s) to be Solved by the Invention] Although some research results are released about composition of a spherical porosity silica until now as above-mentioned, above-mentioned (1) - (7) and (10) use quarternary ammonium salt, such as CTAB which is a surfactant expensive as a reagent which controls pore structure, or they have added other surfactants additionally. Furthermore, If the above (2) is removed, the diameter of a spherical silica meso porous body is 10 micrometers or less, and deals with only the silica pure component further. And the reaction time for producing the organic inorganic nano complex containing the surfactant which is the precursor of the spherical porous body which is an end product will need long duration dozens of hours - three days except for the above (10). Furthermore, when introducing metal components other than Si, in order to make the tetraethyl alt.silicate (TEOS) which is silicate ester, and a stable homogeneity solution phase form, technical problems, like only the meltable limited metal salt can be used are in an expensive metal alkoxide or straight chain alkylamine.

[0007] Moreover, although it is possible to produce the spherical particle of diameter the order of several microns with the sol-gel method which used the metal alkoxide as the start raw material, it is difficult to produce a particle 10 micrometers or more in many cases, and moreover does not have the pore based on skeletal structure, but only the porosity resulting from a particle gap is shown.

[0008] Therefore, this invention aimed at manufacturing the spherical porosity silica particle of micron order by using alkylamine as a control agent of pore structure, and changing the mixed rate of reacting matter, acidity, and the number of carbon of an alkyl chain to the solution which mixed silicate ester and a water miscibility organic solvent in the very simple system of reaction which added water or aqueous acids. Furthermore, the metal salt which dissolved in silicate ester and alcohol is mixed, other metals permute a

part of Si, and the spherical porosity silica thru/or silica metal complex particle which contains a metallic oxide etc. out of a frame is manufactured.
[0009]
[Means for Solving the Problem] this invention persons grow up into a spherical particle the silica-alkylamine compound product which adds water or aqueous acids under stirring, and is generated at mixed liquor including the combination of a water miscibility organic solvent, alkylamine and silicate ester or silicate ester, and a metal salt meltable to a water miscibility organic solvent, as a result of repeating research wholeheartedly, in order to attain the above-mentioned object, and the manufacture approach of the spherical porosity silica characterized by removing the alkylamine in a spherical particle thru/or a silica metal complex particle provides. According to the manufacture approach of this invention, 1. silicate ester and alkylamine are used by the mole ratio of 1:0.1 thru/or 1:0.8, 2. A water miscibility organic solvent is used per [0.05] one mol of silicate ester thru/or in the amount of ten mols, 3. Water is added per [20] one mol of silicate ester thru/or in the amount of 100 mols, 4. Using an acid in the amount of 0.15 mols or less per one mol of silicate ester, 5. water miscibility organic solvent's being alcohol of univalent thru/or many **, and being [6. silicate ester / a carbon number / silicate ester of the alcohol of 1 thru/or 4] ** are desirable. According to this invention, it sets to a spherical porosity silica thru/or a silica metal complex particle again. M expresses polyvalent metal among following type SiO2 and nMOm / 2 types, and m is the valence of polyvalent metal. n is the spherical porosity silica thru/or silica metal complex particle which is 0.1 or less number containing zero and which comes out and has the chemical presentation expressed. The sphericity for which is in the range whose particle size is 0.1 thru/or 500 micrometers, and it asked by the circumscribed circle method is parenchyma top 1. The spherical porosity silica thru/or silica metal complex particle characterized by having an X diffraction peak at an angle of diffraction 1 thru/or 5 times (Cu-Kalpha), and having the maximal value of pore volume in a pole diameter 15 thru/or 40A is offered. As for the spherical porosity silica of this invention thru/or a silica metal complex particle, it is desirable to see with a scanning electron microscope photograph and to consist of a parenchyma top monodisperse particle. According to this invention, the catalyst characterized by consisting of the above-mentioned spherical porosity silica thru/or a silica metal complex particle or catalyst support, a deodorant, and a gas conditioning agent are offered.
[0010]
[Embodiment of the invention] this invention person etc. is the system of reaction which used tetraethyl alt.silicate (it may omit and may be hereafter called TEOS), straight chain alkylamine, and a hydrochloric-acid water solution, and showed clearly that the silica porous body with a spiral-like diameter of 1-6 micrometers in spherical is compoundable in a hollow-like list as he described by (7) of the above-mentioned Prior art. Furthermore, in the same system of reaction as the above-mentioned (7), it was shown that a 5-300-micron spherical porosity silica thru/or a silica metal complex particle are producible by changing the addition sequence of reacting matter.
[0011] In the manufacturing method of the spherical porosity silica of the micron order in this invention thru/or a silica metal complex particle An alkoxide does not need to use an expensive metal alkoxide except Si-alkoxide, using an alkoxide raw material as said silicate ester, Generation of the particle of an irregular configuration is controlled by adding alcohol to the system of reaction, and a spherical porosity silica uniform [particle size distribution] and bigger is obtained, It has marked progressivity on manufacture conditions -- mere water may be able to be substituted for that particle size is controllable and aqueous acids by agitating speed.
[0012] It is the description that the spherical porosity silica of this invention thru/or a silica metal complex particle grow up into a spherical particle the silica-alkylamine compound product which adds water or aqueous acids under stirring into mixed liquor including the combination of a water miscibility organic solvent, alkylamine and silicate ester or silicate ester, and a metal salt meltable to a water miscibility organic solvent, and is generated, and removes and manufactures the alkylamine in a spherical particle.
[0013] according to the manufacture approach of this invention -- silicate ester and alkylamine -- 1:0.1 thru/or 1:0.8 -- desirable -- the mole ratio of 1:0.2 thru/or 1:0.7 -- moreover, a water miscibility organic solvent -- desirable -- the alcohol of univalent thru/or many ** -- per [0.05] one mol of silicate ester -- or ten mols It mixes in 0.1 thru/or the amount of 3.0 mols preferably. After that water Per [20] one mol of silicate ester thru/or 100 mols, By adding in the amount of 25 thru/or 65 preferably, and using preferably 0.15 mols or less per one mol of silicate ester of acids in 0.11 or less amount if needed, the sphericity for which it asked by the circumscribed circle method is parenchyma top 1, and it sees with a scanning electron

microscope photograph, and a parenchyma top monodisperse particle is obtained. Except this range, sphericity is not obtained by the thing of parenchyma top 1 by the particle of an irregular configuration, and the particle which saw and carried out mono dispersion with the scanning electron microscope photograph is not obtained. (Refer to drawing 8 mentioned later)

[0014] According to this invention, it sets to a spherical porosity silica thru/or a silica metal complex particle again. the inside of following type SiO2 and nMOm / 2 types, and M -- polyvalent metal -- desirable -- Ti -- A kind is expressed with being chosen out of Zr, aluminum, Fe, Zn, Cr, Mn, Co, Cu, nickel, V, Sn, etc. that it is few, 0.1 or less number with which m is the valence of polyvalent metal and n contains zero -- it is 0.05 or less preferably -- It is the spherical porosity silica thru/or silica metal complex particle which comes out and has the chemical presentation expressed. Or there are 500 micrometers in 1 thru/or the range of 300 micrometers preferably. particle size -- 0.1 -- The sphericity for which it asked by the circumscribed circle method is parenchyma top 1, and it is the description to offer the spherical porosity silica thru/or silica metal complex particle characterized by having an X diffraction peak at an angle of diffraction 1 thru/or 5 times (Cu-Kalpha), and having the maximal value of pore volume in a pole diameter 15 thru/or 40A.

[0015] As a concrete example of the manufacturing method of the spherical porosity silica particle of this invention, an outline is shown in drawing 1 . Based on the order organization potency of the bottom alkylamine of an alcoholic existence, by adding aqueous acids in a homogeneity transparence solution (A) with TEOS and a metal dissolved kind A silica-alkylamine compound product generates by the cooperative interaction of the ionized alkylamine and the metal dissolved kind containing Si (3 in drawing 1 (B)). The spherical particle which has the macro gestalt of micron order generates by this serving as a nucleus, and a primary particle generating, and carrying out particle growth by the collision between (B) and a primary [further] particle (C). The end product obtained by removing an organic component by processing of heating etc. will have the regularity of the microstructure, i.e., pore structure, formed in the phase of (A), and will have order structure on two different scales at the same time it presents the shape of a ball of micron order. Moreover, since a spherical particle grows by the collision of a primary particle, (progress to C)) and the spherical porosity silica particle obtained serve as a restoration mold in which the primary particle carried out the condensation set from (drawing 1 Naka (B). Furthermore, various metal salts are meltable to alcohol, and can produce the spherical porosity silica metal complex particle containing Ti, Zr, aluminum, Fe, Zn, Cr, Mn, Co, Cu, nickel, V, Sn, etc. Here, alcohol not only promotes solubilization of a metal salt and TEOS, but is presumed to be that which is effective in speeding up the growth to (C) in drawing 1 from (B) by reducing the polarity of a solvent.

[0016] This manufacturing method has the pore arranged periodically, and it can manufacture it under ordinary temperature ordinary pressure for a pole diameter not only to be able to control easily moreover but also the precursor of the spherical porosity silica of micron order and a spherical porosity metal complex particle within 80 minutes. Moreover, it becomes controllable [particle diameter] with agitating speed, acid concentration, or the addition rate of alcohol.

[0017] Drawing 2 is the scanning electron microscope (SEM) photograph of the spherical porosity silica particle ((a), (b)) obtained according to the above-mentioned manufacturing method, and the spherical porosity silica metal complex particle ((c), (d)) containing aluminum. Drawing 3 is X diffraction drawing corresponding to (a) - (d) of drawing 2 , and existence of a base echo shows that it is not irregular-like [a pore array]. moreover, the nitrogen adsorption isotherm corresponding to (a) - (d) of drawing 2 in drawing 4 -- it is -- Horvath-Kawazoe -- (a) showed broadcloth distribution focusing on the average effective diameter of 1.8nm, and the pore system distribution curve for which it asked by law showed that (b) - (d) was carrying out sharp distribution the core [(b)3.21nm, (c)1.85nm, and (d)3.54nm], respectively.

[0018] The ammonia temperature-programmed-desorption spectrum of the spherical porosity silica of this invention thru/or a silica metal complex particle is shown in drawing 5 . From the configuration of a spectrum, a difference is accepted in the amount of solid acid by the solid acid list on the strength with the metal kind to contain. Although the amount of ammonia desorption of Fe is very little, the application as a catalyst of versatility [have / like aluminum / a function as solid acid] is possible for Cr, Zn, etc.

[0019] Since the spherical porosity silica of this invention thru/or a silica metal complex particle can also adsorb a malodorous substance into the meso pore which progressed in excellence, itself has a function as a deodorant. Moreover, it has the silanol group which shows solid acid nature to a front face despite weak reinforcement, and basic malodorous substances, such as ammonia and an amine, are chemisorbed.

[0020] The deordorization test result to the spherical porosity silica of this invention thru/or the

trimethylamine of a silica metal complex particle, an acetaldehyde, ethyl mercaptan, and a hydrogen sulfide is shown in drawing 6 . About the silica metal complex particle, the deordorization property of all types of gas was shown in this Fig. about the spherical porosity silica for the example and the comparison only especially about the complex particle including the metal kind with which the remarkable deordorization effectiveness was accepted. Since the spherical porosity silica of this invention thru/or a silica metal complex particle show high initial adsorption capacity and saturated adsorption to an offensive odor component except for the spherical porosity silica particle to a trimethylamine and ethyl mercaptan, the application as a deodorant is possible.

[0021] The test result of the photocatalyst ability to an acetaldehyde is shown in drawing 7 . This Fig. shows that the spherical porosity silica particle of an example 1 does not have photocatalyst ability, as a result of irradiating ultraviolet rays with a wavelength of 254nm. Moreover, photocatalyst ability remarkable in the spherical porosity silica metal complex particle containing Cr of an example 6 was accepted. Since it has the initial adsorption capacity and photocatalyst ability which were excellent to various gas constituents, the spherical porosity silica metal complex particle of this invention can be used as a photocatalyst for clearance and disassembly of environmental pollution molecules, such as not only an offensive odor component but NOx.

[0022] Furthermore, as a result of measuring the adsorption isotherm of a steam, adsorption capacity with the spherical porosity silica of this invention thru/or a silica metal complex particle remarkable in a pole diameter list at the narrow phase counter pressure of a certain fixed range according to heat-treatment temperature is accepted. For example, since the standup of rapid steam adsorption isotherm is accepted in the phase counter pressure 0.5 neighborhood and it has the amount of adsorption of 430ml (STP) / g by 0.5-0.6 when a spherical porosity silica particle is heat-treated at 800 degrees C for 1 hour, the utilization as a gas conditioning agent is also possible.

[0023] A meltable metal salt is shown in the water miscibility organic solvent, the alkylamine and silicate ester or silicate ester used by this invention, and a water miscibility organic solvent.

[0024] As silicate ester as a silica raw material used by this invention, it is Si-alkoxide and tetraethyl alt.silicate (it omits Following TEOS) is used that it is possible to use tetramethyl alt.silicate, tetraethyl alt.silicate, tetra-isopropyl alt.silicate, tetra-n-butyl alt.silicate, etc. and preferably.

[0025] As a water miscibility organic solvent, a methanol, ethanol, propanol, a butanol, etc. can be used and ethanol is used preferably.

[0026] As alkylamine, straight chain alkylamine is desirable, a thing with 8-18 carbon is used, it is comparatively cheap, and the octyl amine which is in a solution condition in ordinary temperature, and a dodecyl amine are desirable.

[0027] As a metal salt meltable to a water miscibility organic solvent, all meltable metal salts can be used for alcohol, such as a chloride, a nitrate, a sulfate, and its hydrate.

[0028] Moreover, as an acid, a hydrochloric acid, a nitric acid, an acetic acid, etc. can be used.

[0029] while stirring in composition of the spherical porosity silica of this invention thru/or a silica metal complex particle -- TEOS -- alcohol -- it is made to react about 10 to 60 minutes preferably less than 80 minutes at a room temperature, adding 1-alkylamine subsequently, adding aqueous acids after 15 seconds - 5 minutes, and holding sufficient mixed state The mixed mole ratio of a start raw material is TEOS:1-alkylamine:alcoholic:acid:water:metallic element =1:0.1-0.8:0.05-10:0-0.15:20-100:0-0.1.

[0030] When the mixed mole ratio of a start raw material is furthermore described in a detail, in the case of an octyl amine, it is TEOS:octyl amine:ethanol:acid:water =1:0.20-0.45:1.10-2.95:0.030-0.110:25-63 preferably at composition of a spherical porosity silica particle. In the case of a dodecyl amine, it is TEOS:dodecyl amine:ethanol:acid:water =1:0.30-0.65:0.10-2.55:0.002-0.007:25-63 preferably.

[0031] Stirring the metal salt which dissolved in alcohol beforehand, after adding to TEOS, alkylamine is added immediately and it stirs for 1 minute to 20 minutes, aqueous acids are added, continuing stirring further, and it is made to react to composition of the spherical porosity silica metal complex particle which contains other metallic elements in a silica matrix about 10 to 60 minutes preferably less than 80 minutes at a room temperature, holding sufficient mixed state. In the case of an octyl amine, the mixed mole ratio of a start raw material is TEOS:octyl amine:ethanol:metallic element:acid:water =1:0.20-0.45:1.10-2.95:0.001-0.05:0-0.035:25-63 preferably. In the case of a dodecyl amine, it is TEOS:dodecyl amine:ethanol:metallic element:acid:water =1:0.30-0.65:0.65-2.55:0.001-0.025:0-0.004:25-63 preferably.

[0032] the above -- in any case, a solid-state product is separated from the suspension after a reaction, and it is made to dry it enough at room temperature -100 degree C in order to remove an organic

component finally and to produce a spherical porosity silica thru/or a silica metal complex particle, it heat-treats above 500 degrees C preferably above 400 degrees C for 1 hour for 2 hours or more.
[0033] (Application) The spherical porosity silica of this invention thru/or a silica metal complex particle are used as a catalyst or catalyst support, a deodorant, a gas conditioning agent, an adsorbent, etc., and can be used combining an inorganic adsorbent, an antimicrobial agent, a photoreaction nature semi-conductor, etc. according to an application. The spherical porosity silica of this invention thru/or a silica metal complex particle can be easily fabricated in the configuration according to an application if needed by well-known approaches, such as performing extrusion granularity, a cylinder, a pellet type, and in the shape of a honeycomb. moreover, the raw material of these various configurations -- spreading and impregnation -- kneading -- being crowded -- etc. -- it can also add. As a raw material, there are timber, paper, plastics, fiber, inorganic system exterior and interior sheathing material, etc. Moreover, it adds in common coatings and can use broadly as a coating with a gas conditioning function.
[0034] Since the spherical porosity silica thru/or silica metal complex particle used for above-mentioned this invention according to the class of offensive odor component can also adsorb a malodorous substance into the meso pore which progressed in excellence, itself has a function as a deodorant. Moreover, it has the silanol group which shows solid acid nature to a front face despite weak reinforcement, and basic malodorous substances, such as ammonia and an amine, are chemisorbed.
[0035] When using the spherical porosity silica of this invention thru/or a silica metal complex particle as a deodorant, in order to assist the deodorization force, sepiolite, a palygorskite, activated carbon, a zeolite, an activated carbon fiber, sepiolite mixing paper, silica gel, the activated clay, an alumina, a vermiculite, the diatom earth, etc. may be used together. Moreover, it can also consider as a synthetic deodorant combining the deodorant which has deodorization nature to other deodorants, for example, a hydrogen sulfide, methyl mercaptan, ethyl mercaptan, etc. As a deodorant to combine, synthetic FIROKEI acid magnesium and ** aluminum FIROKEI acid zinc are desirable.
[0036] Moreover, as a photoreaction nature semi-conductor, titanium oxide, tungstic oxide, a zinc oxide, cerium oxide, strontium titanate, a niobic acid potassium, etc. are mentioned. the spherical porosity silica of this invention thru/or the silica metal complex particle 100 weight section -- receiving -- a photoreaction nature semi-conductor -- 0.1 -- or 200 weight sections combination can be carried out.
[0037] Furthermore, an antimicrobial agent can be used 0.1 thru/or by carrying out 20 weight sections combination to the spherical porosity silica of this invention thru/or the silica metal complex particle 100 weight section as an antibacterial deodorization gas conditioning agent with the function of antibacterial and deodorization nature. The sustained-release antimicrobial agent which specifically consists of silver system inorganic antimicrobial agents, such as the zeolite which supported silver, an amorphous aluminosilicate, an apatite, a phosphoric-acid zirconium, silica gel, a calcium silicate, and glass, or benzalkonium chloride-silica complex is mentioned.
[0038]
[Example] Next, this invention is not limited by this example although an example explains this invention still more concretely. In addition, each test method performed in the example was performed by the following approach.
[0039] (Measuring method)
(1) Scanning electron microscope : JEOL JSM5300 was used and it observed by the acceleration voltage of 10kV, and WD11mm.
[0040] (2) Specific surface area and pore volume distribution : BELSORP28 made from a Japanese bell was used, it asked for the BET specific surface area from the nitrogen adsorption isotherm which is liquid nitrogen temperature and was measured, and pore volume distribution was analyzed by the Horvath-Kawazoe method.
[0041] (3) Particle size : it measured with the aperture tube of 200-micron meter using Coulter MultisizerII made from the Beckmann coal tar.
[0042] (4) Sphericity : the particle periphery configuration (circumscribed circle) of the typical scanning electron microscope photograph of a particle was observed and searched for.
[0043] (5) X diffraction: -- the Rigaku make -- Rota FREX RU-300 were used and it measured by the source of Cu-K alpha rays, the acceleration voltage of 40kV, and 80mA.
[0044] (6) Ammonia temperature-programmed-desorption spectrum : it measured on condition that the following using the TPD equipment made from a Japanese bell.
Pretreatment 400 degrees C, 1-hour vacuum dearing Ammonia adsorption 100 degrees C, 30 minutes

Clearance of physical-adsorption part ammonia 180 degrees C TPD meaasurement 100-600 degrees C, the programming rate of 10 degrees C / min [0045] (7) Deordorization trial : the concentration change to the initial concentration of 100 ppm of object gas was measured on conditions with a sample 0.1g and a measurement chamber volume of 900ml using the gas detector made from a gas tech.
[0046] (8) Photocatalyst ability trial : using the low pressure mercury lamp, ultraviolet rays with a wavelength of 254nm were irradiated at the above-mentioned deordorization testing device, and concentration change of acetaldehyde gas was measured using the gas detector made from a gas tech.
[0047] (9) Steam adsorption : BELSORP18 made from a Japanese bell was used, and the water vapor content was calculated from the adsorption isotherm measured at 25 degrees C.
[0048] (10) A part for a chemical composition analysis silica (SiO2) was measured with hydrofluoric-acid scorification, and measured by the ICP-AES method after alkali fusion about aluminum, Zr, Fe, Cr, metaled Zn, and metaled (M) Sn.
[0049] (Example 1) TEOS is stirred by 600rpm, and a hydrochloric-acid water solution is added after adding ethanol and an octyl amine, and it stirs as it is for 1 hour. the mole ratio of a mixed solution -- TEOS:octyl amine: -- ethanol: -- HCl: -- water = -- it is 1:0.34:1.94:0.068:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica particle is produced. The median diameter of a generation spherical porosity silica particle is 34.9 micrometers, and specific surface area shows 955m2/g. Moreover, an analysis result is shown in a table 4.
[0050] (Example 2) TEOS is stirred with constant speed, and a hydrochloric-acid water solution is added after adding ethanol and a dodecyl amine, and it stirs as it is for 1 hour. the mole ratio of a mixed solution -- TEOS:dodecyl amine: -- ethanol: -- HCl: -- water = -- it is 1:0.35:0.87:0.004:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica particle is produced. Moreover, the spherical porosity silica particle from which particle size differs will be obtained, and if agitating speed is changed using the mixing ratio of reacting matter as the same, as shown in a table 1, a median diameter will change with agitating speed notably.
[0051]
[A table 1]
Rotational frequency (rpm) Median diameter (micrometer) Specific surface area (m2/g)
Example 2-1 400 73.9 917 examples 2-2 600 53.5 927 examples 2-3 800 32.1 979 examples 2-4 1000 22.1 984 [0052] (Example 3) After stirring TEOS by 600rpm, adding an octyl amine and stirring after addition AlCl3.6H2O dissolved in ethanol for 20 minutes, water or a hydrochloric-acid water solution is added, and it stirs further as it is for 1 hour. the mole ratio of a mixed solution -- TEOS:octyl amine: -- ethanol: -- aluminum:HCl: -- water = -- it is 1:0.34:1.19:0.023:0 to 0.07:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. Moreover, by this system of reaction, even if it changes the mixed mole ratio of a hydrochloric-acid water solution, a spherical porosity silica metal complex particle is obtained, and a median diameter, specific surface area, etc. are shown in a table 2.
[0053]
[A table 2]
Mixing of a hydrochloric acid Median diameter (micrometer) Specific surface area (m2/g)
Mole-ratio example 3-1 0 (pure water) 38.7 1013 examples 3-2 0.0007 ~ 960 examples 3-3 0.007 ~ 954 examples 3-4 0.035 33.3 948 examples 3-5 0.07 ~ 877 [0054] (Example 4) After stirring TEOS by 600rpm, adding a dodecyl amine and stirring after addition AlCl3.6H2O dissolved in ethanol for 3 minutes, water is added and it stirs further as it is for 1 hour. the mole ratio of a mixed solution -- TEOS:dodecyl amine: -- ethanol: -- aluminum: -- water = -- it is 1:0.34:1.16 to 1.36:0.004:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. As shown in a table 3, it turns out that the median diameter of a generation spherical porosity silica metal complex particle changes with the differences in few mixing ratios of ethanol notably. Moreover, an analysis result is shown in a table 4.
[0055]
[A table 3]

Ethanol Median diameter (micrometer) Specific surface area (m2/g)
a mol — a mixing ratio — example 4-1 1.16 16.6 869 examples 4-2 1.36 19.1 902 [0056] (Example 5) After stirring TEOS by 600rpm, adding an octyl amine and stirring after addition ZrOCl2.8H2O dissolved in ethanol for 10 minutes, a hydrochloric-acid water solution is added and it stirs further as it is for 1 hour. the mole ratio of a mixed solution — TEOS:octyl amine: — ethanol: — Zr:HCl: — water = — it is 1:0.35:1.18:0.017:0.034:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. The median diameter of a generation spherical porosity silica metal complex particle is 63.4 micrometers, and specific surface area is 822m2/g. Moreover, an analysis result is shown in a table 4.
[0057] (Example 6) After stirring TEOS by 600rpm, adding an octyl amine and stirring after addition CrCl3.6H2O dissolved in ethanol for 10 minutes, a hydrochloric-acid water solution is added and it stirs further as it is for 1 hour. the mole ratio of a mixed solution — TEOS:octyl amine: — ethanol: — Cr:HCl: — water = — it is 1:0.34:1.18:0.01:0.034:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. The median diameter of a generation spherical porosity silica metal complex particle is 39.0 micrometers, and specific surface area is 774m2/g. Moreover, an analysis result is shown in a table 4.
[0058] (Example 7) After stirring TEOS by 600rpm, adding an octyl amine and stirring after addition FeCl3.6H2O dissolved in ethanol for 10 minutes, a hydrochloric-acid water solution is added and it stirs further as it is for 1 hour. the mole ratio of a mixed solution — TEOS:octyl amine: — ethanol: — Fe:HCl: — water = — it is 1:0.34:1.17:0.01:0.068:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. Moreover, an analysis result is shown in a table 4.
[0059] (Example 8) TEOS is stirred by 600rpm, and after adding ZnCl2 dissolved in ethanol, after adding an octyl amine and stirring for 10 minutes, a hydrochloric-acid water solution is added and it stirs further as it is for 1 hour. the mole ratio of a mixed solution — TEOS:octyl amine: — ethanol: — Zn:HCl: — water = — it is 1:0.35:1.18:0.02:0.069:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. Moreover, an analysis result is shown in a table 4.
[0060] (Example 9) After stirring TEOS by 600rpm, adding an octyl amine and stirring after addition SnCl4 and 5H2O dissolved in ethanol for 10 minutes, a hydrochloric-acid water solution is added and it stirs further as it is for 1 hour. the mole ratio of a mixed solution — TEOS:octyl amine: — ethanol: — Sn:HCl: — water = — it is 1:0.35:1.18:0.01:0.034:38. After carrying out a solid-state product a ** exception from the suspension after a reaction and making it dry enough at 50 degrees C, it heats at 600 degrees C for 1 hour, an organic component is removed, and a spherical porosity silica metal complex particle is produced. A mosquito metal complex particle is obtained and a median diameter, specific surface area, etc. are shown in a table 2.
[0061]
[A table 4]

	酸化物の種類	金属－Si	仕込み 金属酸化物のモル比 /SiO_2	n値 生成物に含まれる金属酸化物のモル比 /SiO_2
実施例1		Si	0	0
実施例4	Al_2O_3	Al-Si	0.002	0.002
実施例5	ZrO_2	Zr-Si	0.017	0.015
実施例6	Cr_2O_3	Cr-Si	0.005	0.005
実施例7	Fe_2O_3	Fe-Si	0.005	0.005
実施例8	ZnO	Zn-Si	0.02	0.015
実施例9	SnO_2	Sn-Si	0.01	0.005

[0062] (Example 1 of a comparison) The description of this manufacturing method was adding ethanol to a solvent, and it performed the same composition as an example 1 by ethanol additive-free in order to show the addition effectiveness. Although a difference is hardly accepted in specific surface area or X diffraction

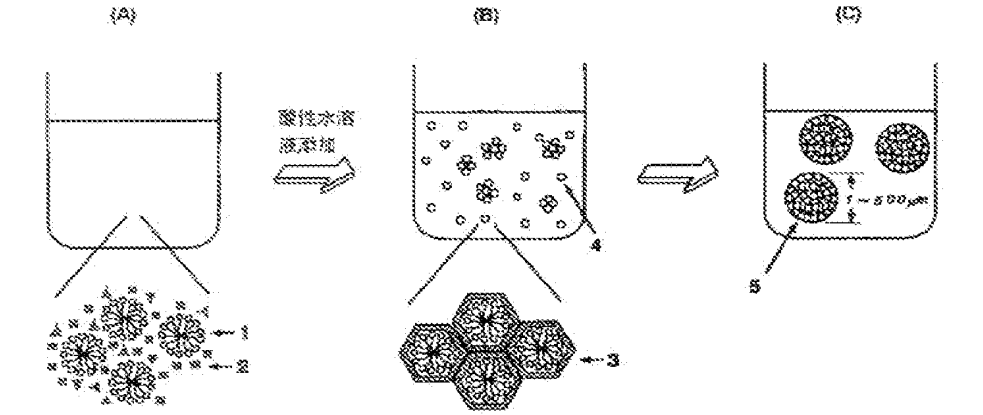
drawing by the existence of addition of ethanol, addition of ethanol shows that generation of the particle of an irregular configuration is controlled so that clearly from the SEM photograph of drawing 8 .
[0063]
[Effect of the Invention] In the very simple system of reaction which alkylamine was used for this invention as a control agent of pore structure, and added water or aqueous acids to the mixed solution of TEOS and alcohol By changing the mixed rate of reacting matter, acidity, and the number of carbon of an alkyl chain The organic inorganic nano complex containing the surfactant which serves as a precursor of a spherical porous body under ordinary temperature and ordinary pressure is produced for a short time, and the manufacture approach of the spherical porosity silica particle of the micron order covering the diameter of several microns ~ hundreds of microns by removing the organic substance eventually is offered. Furthermore, after mixing with TEOS the metal salt which dissolved in alcohol, other metals permute a part of Si with the homogeneity solution alkylamine and by subsequently adding water or aqueous acids, and the manufacture approach of the spherical porosity silica metal complex particle of the micron order containing a metallic oxide etc. is offered out of a frame. And with the order nature of the macro gestalt of being spherical, simultaneously, 15~40A pore has had and arranged regularity, and the manufacturing method of the high specific-surface-area spherical porosity silica which has regularity on two different scales thru/or a silica metal complex particle is offered. Since configuration selection ability is demonstrated since it furthermore has the homogeneity of high specific surface area and a pole diameter, and the trap of various useful or harmful molecules and the ion can be carried out efficiently, it is utilizable for industry and a molecule sieve useful by both sides of environmental protection, catalyst support, and a catalyst pan as a manufacturing method of functional-ceramics raw materials, such as a sensor. Especially, taking advantage of the property of the spherical particle of micron order, it is worthy as a manufacturing method of not only the fixed bed but the catalyst and catalyst support for chemical processes for a fluid bed reaction, or the column packing material for chromatography separation.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the mimetic diagram showing the manufacturing method of the spherical porosity silica of this invention thru/or a silica metal complex particle.
[Drawing 2] It is the scanning electron microscope photograph of the spherical porosity silica metal complex particle containing aluminum of the spherical porosity silica particle of an example 1 (a) and an example 2-2 (b) and an example 3-4 (c), and an example 4-1 (d).
[Drawing 3] It is X diffraction pattern drawing of the spherical porosity silica metal complex particle containing aluminum of the spherical porosity silica particle of an example 1 and an example 2-2 and an example 3-4, and an example 4-1.
[Drawing 4] It is the nitrogen adsorption isotherm of the spherical porosity silica metal complex particle containing aluminum of the spherical porosity silica particle of an example 1 and an example 2-2 and an example 3-4, and an example 4-1. Void is adsorption and continuous tone is the desorption constant-temperature line.
[Drawing 5] It is the ammonia temperature-programmed-desorption spectrum of the spherical porosity silica metal complex particle (example 3-4 (**); example 4-1 (<>)) containing aluminum, the spherical porosity silica metal complex particle (example 6 (O)) containing Cr, the spherical porosity silica metal complex particle (example 7 (**)) containing Fe, and the spherical porosity silica metal complex particle (example 8 (-)) containing Zn.
[Drawing 6] It is the deordorization test result of the spherical porosity silica particle of an example 1 (**, **, -, <>) and the spherical porosity silica metal complex particle (**, <>) containing Cr of an example 6, the spherical porosity silica metal complex particle (O) containing Zn of an example 8, and the spherical porosity silica metal complex particle (**) containing Sn of an example 9.
[Drawing 7] It is the photocatalyst ability test result of the spherical porosity silica particle of an example 1 (**), and the spherical porosity silica metal complex particle containing Cr of an example 6 (O).
[Drawing 8] It is the scanning electron microscope photograph of the spherical porosity silica particle of the example 1 of a comparison.

Drawing selection drawing 1



アルキルアミン（1）とTEOS（2）の均質透明溶液。ただし、（1）の疎水性効果により、（2）が（1）を取り囲んで複合構造体を形成する。

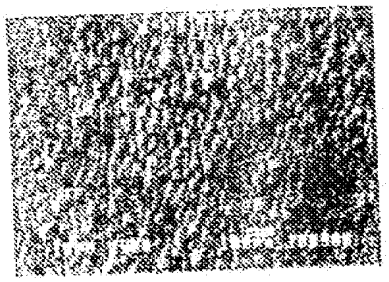
塩性水溶液の添加で（3）の様なアミンを取り囲んだシリカ複数個の集合体（有機無機メソ構造体）をユニットとする核が生成し、1次粒子（4）に成長する。

1次粒子（4）間の凝集によって、ミクロンオーダーの球状粒子（5）となる。

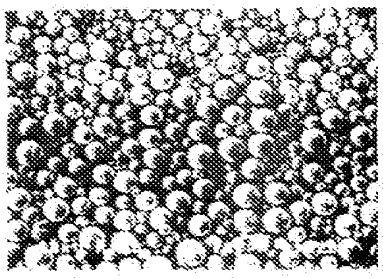
球状多孔質シリカ粒子の生成機構

[Translation done.]

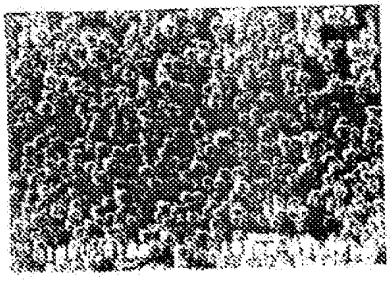
Drawing selection drawing 2



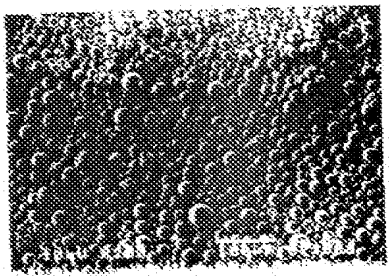
（a）実施例１



（b）　実施例２－２



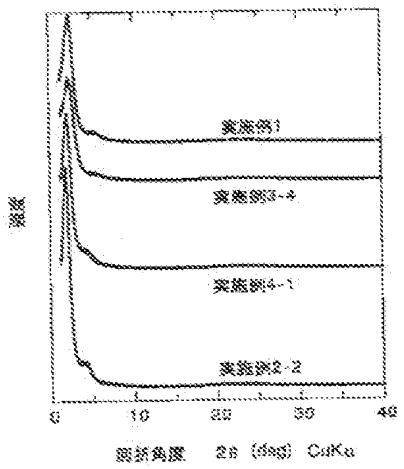
（c）　実施例３－４



（d）　実施例４－１

[Translation done.]

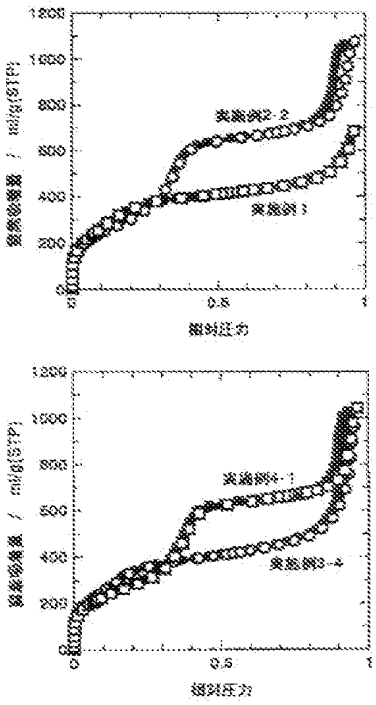
Drawing selection drawing 3



X線回折パターン図

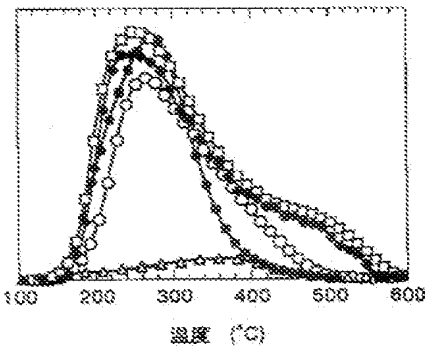
[Translation done.]

Drawing selection drawing 4



[Translation done.]

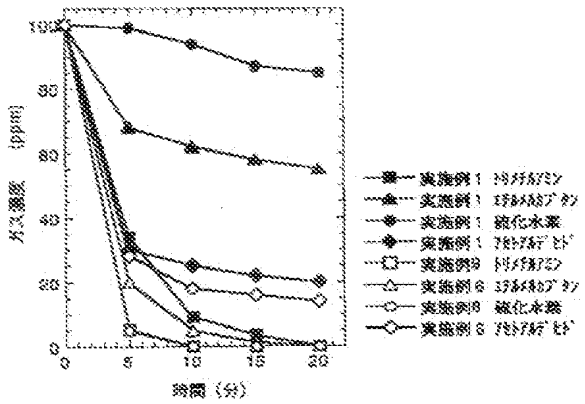
Drawing selection drawing 5



アンモニア昇温脱離スペクトル

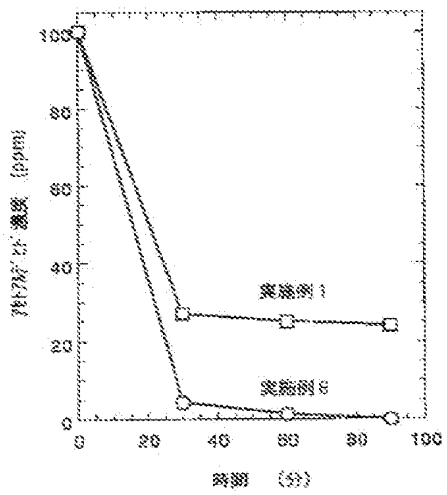
[Translation done.]

Drawing selection drawing 6



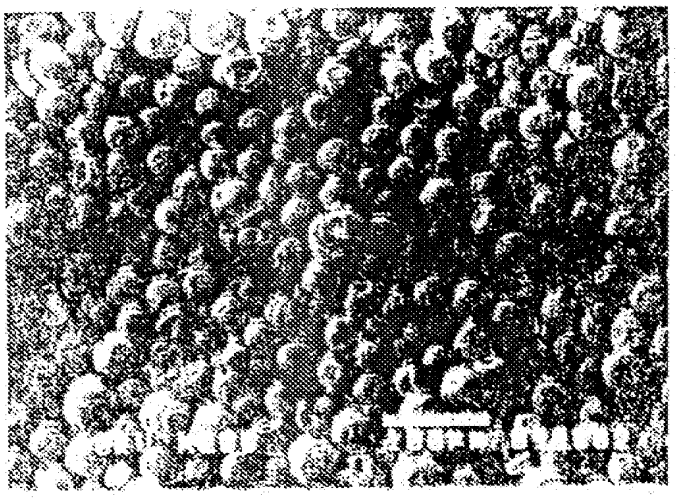
[Translation done.]

Drawing selection drawing 7



[Translation done.]

Drawing selection drawing 8



比較例 1

[Translation done.]